CERTIFICATION OF TRANSLATION

I, *Hye-young Jang*, an employee of Y.P.LEE, MOCK & PARTNERS of Koryo Bldg., 1575-1 Seocho-dong, Seocho-gu, Seoul, Republic of Korea, hereby declare under penalty of perjury that I understand the Korean language and the English language; that I am fully capable of translating from Korean to English and vice versa; and that, to the best of my knowledge and belief, the statement in the English language in the attached translation of *Korean Patent Application No. 10-2004-0052612* consisting of 29 pages, have the same meanings as the statements in the Korean language in the original document, a copy of which I have examined.

Signed this 18th day of December 2009

Hye-young Jang

ABSTRACT

[Abstract of the Disclosure]

A method of producing a cyclic olefin polymer having a polar functional group and a high molecular weight with a high yield in which a catalyst is not deactivated due to polar functional groups. According to the olefin polymerization method, deactivation of a catalyst due to polar functional groups of monomers can be prevented, and thus a polyolefin having a molecular weight of equal to or greater than 100,000 can be prepared with a polymerization yield of equal to or greater than 60%, and the ratio of catalyst to monomer can be in the range of 1/5000 to 1/20,000 due to good activity of the catalyst, and thus removal of catalyst residues is not required.

S P E C I F I C A T I O N

[Title of the Invention]

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METHOD FOR POLYMERIZING CYCLIC OLEFIN HAVING POLAR FUNCTIONAL GROUP, OLEFIN POLYMER PRODUCED BY THE METHOD AND OPTICAL ANISOTROPIC FILM COMPRISING THE SAME

10   [Detailed Description of the Invention]

[Object of the Invention]

[Technical Field of the Invention and Related Art prior to the Invention]

The present invention relates to a cyclic olefin polymer, and more particularly, to a method of producing cyclic olefin polymers having polar functional groups, olefin

15   polymers produced using the method, and an optical anisotropic film comprising the same.

Inorganic materials such as silicon oxides or nitrides have been mainly utilized in the information and electronic industries. Recent technical developments and demands for compact and high efficiency devices need new high performance materials.

20   In this respect, a great deal of attention has been paid to polymers which have desirable physicochemical properties such as low dielectric constant and moisture absorption rate, high adhesion to metals, strength, thermal stability and transparency, and a high glass transition temperature ($T_g > 250$ ℃).

Such polymers can be used as insulating layers of semiconductors or TFT-LCDs,

25   protecting films for polarizing plates, multichip modules, integrated circuits (ICs), printed circuit boards, molding materials for electronic components or electronic materials for flat panel displays, etc.

As one of new performance materials, cyclic olefin polymers which are composed of cyclic olefin monomers such as norbornenes exhibit much more improved

30   properties than conventional olefin polymers, in that they show high transparency, heat

resistance and chemical resistance, and have a low birefringence and moisture absorption rate. Thus, they can be applied to various applications, e.g., optical components such as CDs, DVDs and POFs (plastic optical fibers), information and electronic components such as capacitor films and low-dielectrics, and medical

5   components such as low-absorbent syringes, blister packagings, etc.

Cyclic olefin polymers are known to be prepared by one of the following three methods: ROMP (ring opening metathesis polymerization), copolymerization with ethylene, and addition polymerization using catalysts containing transition metals such as Ni and Pd. These methods are depicted in Reaction Scheme 1 below. Depending

10   on the central metal, ligand and cocatalyst of a catalyst used in the polymerization reaction, polymerization characteristics and the structure and characteristics of polymers to be obtained may be varied.

Reaction Scheme 1
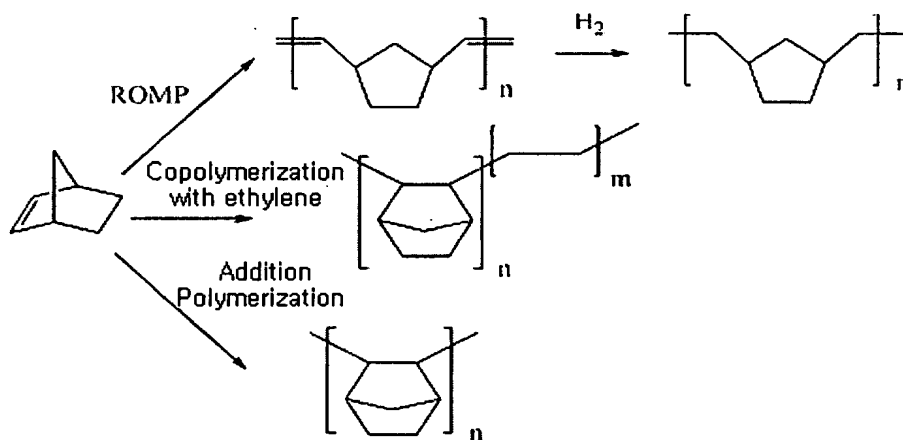
15   In ROMP, a metal chloride such as $TiCl_4$ or WCl_6 or a carbonyl-type organometallic compound reacts with a cocatalyst such as Lewis acid, R_3Al or Et_2AlCl to form active catalyst species such as a metal carbene or a metallocyclobutane which react with double bonds of olefin to provide a ring opened product having double bonds (Ivin, K. J.; O'Donnel, J. H.; Rooney, J. J.; Steward, C. D. Makromol. Chem. 1979, Vol.

20   180, 1975). A polymer prepared by the ROMP method has one double bond per one monomeric repeating unit, thus, the polymer has poor thermal and oxidative stability

and is mainly used as thermosetting resins.

In order to improve physicochemical properties of polymers prepared by the ROMP method, a method of hydrogenation of the ROMP-polymer in the presence of Pd or Raney-Ni catalysts has been proposed. Hydrogenated polymer shows improved oxidative stability, but still needs to be improved in its thermal stability. Further, a cost increased due to additional processes is against its commercial application.

Ethylene-norbornene copolymers are known to be first synthesized using a titanium-based Ziegler-Natta catalyst by Leuna, Corp., (Koinzer, P. et al., DE Patent No. 109,224). However, impurities remaining in the copolymer deteriorates its transparency and its glass transition temperature (T_g) is very low, i.e., 140 ℃ or lower.

As to the addition polymerization of cyclic olefinic monomers, Gaylord et al. reported a polymerization of norbornene using $[Pd(C_6H_5CN)Cl_2]_2$ as a catalyst (Gaylord, N.G.; Deshpande, A.B.; Mandal, B.M.; Martan, M. J. Macromol. Sci.-Chem. 1977, A11(5), 1053-1070). Furthermore, Kaminsky et al. reported a homopolymerization of norbornene using a zirconium-based metallocene catalyst (Kaminsky, W.; Bark, A.; Drake, I. Stud. Surf. Catal. 1990, Vol. 56, 425). These polymers have a high crystallinity, thermally decompose at a high temperature before they melt, and are substantially insoluble in general organic solvents.

Adhesion of polymers to inorganic surfaces such as silicon, silicon oxide, silicon nitride, alumina, copper, aluminium, gold, silver, platinum, nickel, tantalium, and chromium is often a critical factor in the reliability of the polymer for use as electronic materials. The introduction of functional groups into norbornene monomers enables the control of chemical and physical properties of a resultant norbornene polymer.

U.S. Patent No. 3,330,815 discloses a method of polymerizing norbornene monomers having a polar functional group. However, the catalyst is deactivated by polar functional groups of norbornene monomers, which results in an earlier termination of the polymerization reaction, thereby producing a norbornene polymer having a molecular weight of 10,000 or less.

In addition, U.S. Patent No. 5,705,503 discloses a method of polymerizing

norbornene monomers having a polar functional group using $((Allyl)PdCl)_2/AgSbF_6$ as a catalyst. However, an excess of the catalyst is required (1/100 to 1/400 molar ratio relative to the monomer) and the removal of the catalyst residues after polymerization is difficult, which causes the transparency of the polymer to be deteriorated due to a subsequent thermal oxidation.

In addition, Sen et al. reported a method for polymerizing various ester norbornene monomers in the presence of a catalyst, $[Pd(CH_3CN)_4][BF_4]_2$, in which exo isomers were selectively polymerized, and the polymerization yield was low. (Sen et al., *J. Am. Chem. Soc.* 1981, Vol. 103, 4627-4629). In addition, a large amount of the catalyst is used (the ratio of catalyst to monomer is 1:100 to 1:400) and it is difficult to remove catalyst residues after the polymerization.

Recently, U.S. Patent No. 6,455,650 issued to Lipian et al. discloses a method of polymerizing norbornene monomers having a functional group in the presence of a small amount of a catalyst, $[(R')_zM(L')_x(L'')_y]_b[WCA]_d$. However, the product yield in a polymerization of a polar monomer such as an ester-norbornene, is only 5%. Thus, this method is not suitable for the preparation of polymers having polar functional groups.

In addition, Sen et al. reported a method for polymerizing an ester-norbornene in the presence of a catalyst system including $[(1,5-Cyclooctadiene)(CH_3)Pd(Cl)]$, PPh_3, and $Na^+[3,5-(CF_3)_2C_6H_3]_4B^-$, in which the polymerization yield of ester-norbornenes is 40% or lower, the molecular weight of the polymer is 6,500 or lower, and the molar amount of the catalyst used is about 1/400 based on the monomer (Sen et al., Organometallics 2001, Vol. *20*, 2802-2812).

As described above, the polymerization yield, the molecular weight of the obtained polymer, the amount of the catalyst according to the conventional method of polymerizing a cyclic olefin including a polar functional group are not satisfactory. Particularly, the catalyst structure is inactivated by the polar functional group and thermal stability thereof is deteriorated, and thus cannot be used for polymerization at high temperature.

Therefore, there is still a demand for an addition-polymerization of cyclic olefins having polar functional groups which is able to meet a certain desired level in the aspect of polymerization yield, a molecular weight of a resultant polymer, and a molar ratio of a catalyst to monomers.

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[Technical Goal of the Invention]

The present invention provides a method for producing a cyclic olefin polymer having polar functional groups and a high molecular weight in a high yield by using a catalyst which is not deactivated due to polar functional groups.

10 The present invention also provides a cyclic olefin polymer having polar functional groups, which has a high glass transition temperature and a desirable thermal and oxidative stability, a desirable chemical resistance and adhesion to metal.

The present invention also provides an optical anisotropic film made from a cyclic olefin polymer having polar functional groups.

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[Structure and Operation of the Invention]

According to an aspect of the present invention, there is provided a method of producing cyclic olefin polymers having polar functional groups, which comprises:

preparing a catalyst mixture including:

20 i) a procatalyst represented by formula (1) containing a Group 10 metal;

ii) a cocatalyst represented by formula (2) including a salt compound which comprises phosphonium; and

addition-polymerizing cyclic monomers having polar functional groups in the presence of an organic solvent and the catalyst mixture, at a temperature of 80-150 ℃:
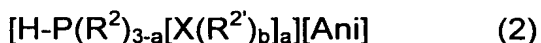
25 $$(R^0)_x(R^1)_yM \qquad (1)$$

wherein R^0 and R^1 are each independently a hydrogen; a halogen; a linear or branched C_{1-20} alkyl or alkenyl; an optionally substituted C_{5-12} cycloalkyl; an optionally substituted C_{6-40} aryl; an optionally substituted C_{7-15} aralkyl; a linear or branched C_{1-20} heteroalkyl or heteroalkenyl including one hetero atom selected from the group

6

consisting of Si, Ge, S, O and N; a C_{6-40} heteroaryl or C_{7-15} heteroaralkyl including one hetero atom selected from the group consisting of Si, Ge, S, O and N; a linear or branched C_{1-20} haloalkyl or haloalkenyl; a linear or branched C_{3-20} haloalkynyl; and an optionally substituted C_{6-40} haloaryl, wherein each substituent is a halogen or a C_{1-20} haloalkyl;

M is a Group 10 metal; and

x and y are each independently an integer from 1 to 2, and

$$[H\text{-}P(R^2)_{3\text{-}a}[X(R^{2'})_b]_a][Ani] \qquad (2)$$
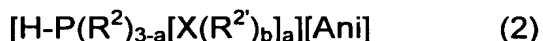
wherein a is an integer from 0 to 3;

X is O, S, Si, or N;

b is 1 if X is O or S, 2 if X is N, and 3 if X is Si;

R^2 and $R^{2'}$ are each independently a hydrogen; a linear or branched C_{1-20} alkyl, alkoxy, allyl, alkenyl or vinyl; an optionally substituted C_{3-12} cycloalkyl; an optionally substituted C_{6-40} aryl; an optionally substituted C_{7-15} aralkyl; a C_{3-20} alkynyl; a tri(linear or branched C_{1-10} alkyl)silyl; a tri(linear or branched C_{1-10} alkoxy)silyl; a tri(optionally substituted C_{3-12} cycloalkyl)silyl; a tri(optionally substituted C_{6-40} aryl)silyl; a tri(optionally substituted C_{6-40} aryloxy)silyl; a tri(linear or branched C_{1-10} alkyl)siloxy; a tri(optionally substituted C_{3-12} cycloalkyl)siloxy; or a tri(optionally substituted C_{6-40} aryl)siloxy, in which each substituent is a halogen or C_{1-20} haloalkyl; and

[Ani] is an anion capable of weakly coordinating to the metal M of Formula 1 and is selected from the group consisting of borate, aluminate, [SbF$_6$]-, [PF$_6$]-, [AsF$_6$]-, perfluoroacetate([CF$_3$CO$_2$]-), perfluoropropionate([C$_2$F$_5$CO$_2$]-), perfluorobutyrate([CF$_3$CF$_2$CF$_2$CO$_2$]-), perchlorate([ClO$_4$]-), p-toluenesulfonate([p-CH$_3$C$_6$H$_4$SO$_3$]-), [SO$_3$CF$_3$]-, boratabenzene, and carborane optionally substituted with a halogen.

According to another aspect of the present invention, there is provided a cyclic olefin polymer having a polar functional group, produced using the above method.

According to another aspect of the present invention, there is provided an optical anisotropic film including a cyclic olefin polymer having a polar functional group.

Herein, the present invention will be described in more detail.

According to the method of producing a cyclic olefin polymer having a polar functional group, the deactivation of a catalyst due to a polar functional group of the monomer can be prevented, the catalyst has high activity, thereby a high yield and a high molecular weight of the cyclic olefin polymer can be achieved with a small amount of the catalyst and the removal process of the catalyst residue is not required.

In the case of general organometallic polymerization catalysts, when the polymerization temperature increases, the polymerization yield increases, whereas a molecular weight of a polymer decreases or catalysts lose the polymerization activity by thermal decomposition (Kaminsky et al. Angew. Chem. Int. Ed., 1985, vol 24, 507; Brookhart et al. Chem. Rev. 2000, vol 100, 1169; Resconi et al. Chem. Rev. 2000, vol 100, 1253).

Meanwhile, a polar group of a norbornene monomer interacts with the catalyst at room temperature to prevent the double bond of a norbornene from coordinating to an active site of the catalyst, thereby resulting in decrease in the polymerization yield and the molecular weight. However, when the polymerization temperature increases, the double bond of a norbornene is easy to insert into the metal-growing polymer chain bond to increase the activity and a β-hydrogen of a growing polymer chain bonded to the metal cannot form a stereo structural environment to be eliminated where it can interact with the catalyst in view of inherent properties of the norbornene monomer, thereby increasing the molecular weight of the polymer (Kaminsky et al. Macromol. Symp. 1995, vol 97, 225). Thus, it is necessary to increase the polymerization temperature. However, most catalysts conventionally used to produce polynorbornenes having polar functional groups tend to be decomposed at 80℃ or higher, and thus polymers having high molecular weights cannot be obtained in a high yield.

However, the catalyst of the present embodiment is thermally stable not to be decomposed at 80℃ or higher and prevents the interaction between the polar functional group of the norbornene monomer and the cationic catalyst, and thus a catalyst active site can be formed or recovered, thereby producing a high molecular

weight cyclic olefin polymer having a polar functional group in a high yield. When the polymerization temperature is higher than 150℃, catalyst components are decomposed in solution, and thus it is difficult to produce a cyclic olefin polymer having a polar functional group and a high molecular weight in a high yield.

5   The catalyst mixture including (i) a procatalyst represented by formula (1) containing a Group 10 metal and a ligand containing hetero atoms bonded to the metal and (ii) a cocatalyst represented by formula (2) including a salt compound which is capable of providing a phosphonium cation and an weakly coordinating anion is not decomposed at the polymerization temperature of 80-150℃ and shows high activity.

10   Borate or aluminate of formula (2) may be an anion represented by formula (2a) or (2b):

$$[M'(R^3)_4] \qquad (2a),$$

$$[M'(OR^3)_4] \qquad (2b)$$

In Formulae (2a) and (2b)

15   M' is boron or aluminum;

R^3 is a halogen; a linear or branched C_{1-20} alkyl or alkenyl optionally substituted with a halogen; a C_{3-12} cycloalkyl optionally substituted with a halogen; a C_{6-40} aryl optionally substituted with a C_{3-20} hydrocarbon; a C_{6-40} aryl optionally substituted with a linear or branched C_{3-20} trialkylsiloxy or a linear or branched C_{18-48} triarylsiloxy; and a

20   C_{7-15} aralkyl optionally substituted with a halogen.

The phosphonium compound used as the cocatalyst in the method has an electronically stabilizing ability and thermally and chemically activates transition metal compounds. In the method, the molar ratio of the cocatalyst to the procatalyst containing Group 10 transition metal is in the range of 0.5:1-10:1. When the molar ratio

25   of the cocatalyst to the procatalyst is less than 0.5:1, the effect of activating the procatalyst is inefficient. When the molar ratio of the cocatalyst to the procatalyst is greater than 10:1, an excess of phosphonium compound coordinates to the metal to prevent a norbornene monomer from coordinating to the metal and the cationic catalyst active species is too electronically stabilized to interact with the double bond of a

9

norbornene monomer, thereby resulting in decreasing both polymerization yield and molecular weight.

The catalyst mixture including the procatalyst and the cocatalyst may be supported on a fine particulate support. The fine particulate support may be silica, titania, silica/chromia, silica/chromia/titania, silica/alumina, aluminum phosphate gel, silanized silica, silica hydrogel, montmorillonite clay or zeolite. When the catalyst mixture is supported on the find particulate support, a molecular weight distribution of a polymer can be controlled by selecting inorganic support and the polymer morphology can be improved.

The catalyst mixture can be directly used in a solid phase without a solvent or can be mixed in a solvent to form a preformed catalyst in the form of a mixture or a complex of the respective catalyst components, i.e. the Group 10 metal compound and the phosphonium compound. Further, each catalyst components can be directly added into the polymerization reaction system without being preformed. When the catalyst mixture is dissolved in a solvent, dichloromethane, dichloroethane, toluene, chlorobenzene or a mixture thereof can be used as the solvent.

The total amount of the organic solvent in the reaction system may be 50-800%, and preferably 50-400%, by weight of based on the total monomer in the monomer solution. When the total amount of the organic solvent in the reaction system is less than 50% based on the weight of the total monomer in the monomer solution, the mixing in the polymerization reaction is difficult due to high viscosity of the polymer solution. When the total amount of the organic solvent in the reaction system is greater than 800% based on the weight of the total monomer in the monomer solution, both the polymerization yield and the molecular weight are reduced due to slow polymerization rate.
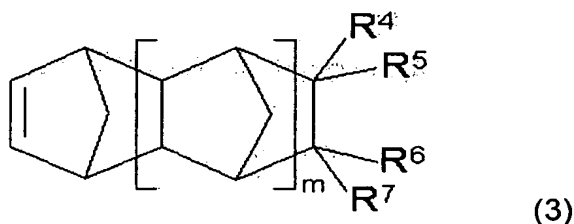
In the polymerization reaction system, the molar ratio of the catalyst mixture based on the Group 10 transition metal compound to the monomers contained in the monomer solution is in the range of 1:2,500 - 1:200,000. This ratio of the catalyst to the monomers is far smaller than that used in conventional polymerization reaction system

for preparing a polar cyclic olefin polymer, however it is sufficient to exhibit catalytic activity in the method of the present invention for preparing a high molecular weight of a cyclic olefin polymer. Preferably, the molar ratio of the catalyst system to the monomers is in the range of 1: 5,000~1: 20,000.

5   A monomer used to prepare the cyclic olefin polymer having a polar functional group used in the method is a norbornene-based monomer having a polar functional group. A norbornene-based monomer or norbornene derivative indicates a monomer having at least one norbornene (bicyclo[2.2.2]hept-2-ene) unit.

A homopolymer may be prepared by polymerizing same norbornene-based

10   monomer containing a polar functional group, or a copolymer including di- and tri-copolymers may be prepared by polymerizing different polar functional norbornene-based monomers, or a copolymer including di- and tri-copolymers may be prepared by polymerizing a polar functional norbornene-based monomer and a norbornene monomer having non-polar functional group.

15   The norbornene-based monomer including the polar functional group may be represented by Formula 3 below.
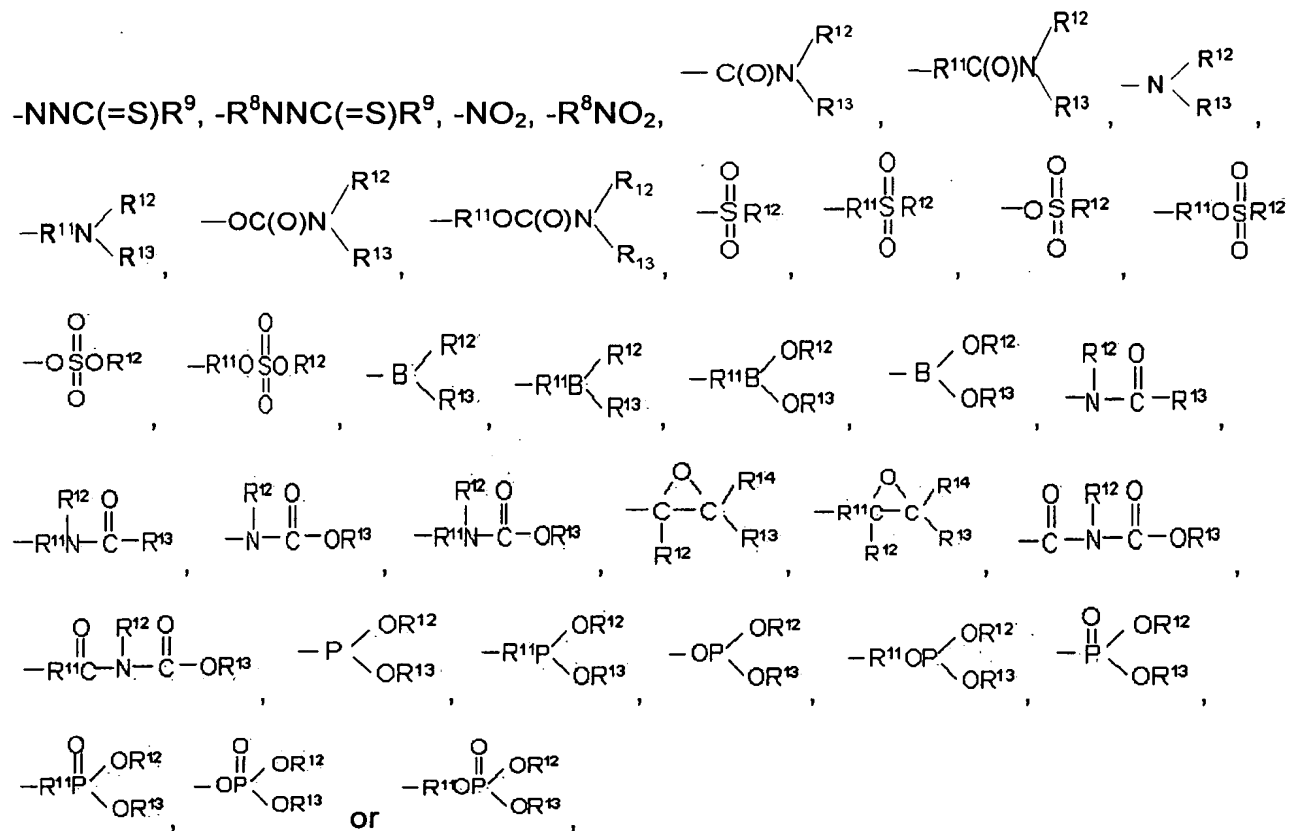

(3)

where m is an integer from 0 to 4;at least one of R^4, R^5, R^6, and R^7 is a polar functional group, and the others are nonpolar functional groups, wherein R^4, R^5, R^6, and

20   R^7 can be bound to each other to form a saturated or unsaturated C_{4-12} cyclic group or a C_{6-24} aromatic ring;

in which the nonpolar functional group is a hydrogen; a halogen; a linear or branched C_{1-20} alkyl, haloalkyl, alkenyl or haloalkenyl, a linear or branched C_{3-20} alkynyl or haloalkynyl; a C_{3-12} cycloalkyl optionally substituted by an alkyl, an alkenyl, an alkynyl,

25   a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; a C_{6-40} aryl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; or a

C_{7-15} aralkyl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; and

the polar functional group is a non-hydrocarbonaceous polar group having at least one O, N, P, S, Si or B and is $-OR^9$, $-OC(O)OR^9$, $-R^8OC(O)OR^9$, $-C(O)R^9$,

5 $-R^8C(O)R^9$, $-OC(O)R^9$, $-R^8OC(O)R^9$, $-(R^8O)_k-OR^9$, $-(OR^8)_k-OR^9$, $-C(O)-O-C(O)R^9$,

$-R^8C(O)-O-C(O)R^9$, $-SR^9$, $-R^8SR^9$, $-SSR^8$, $-R^8SSR^9$, $-S(=O)R^9$, $-R^8S(=O)R^9$, $-R^8C(=S)R^9$,

$-R^8C(=S)SR^9$, $-R^8SO_3R^9$, $-SO_3R^9$, $-R^8N=C=S$, $-NCO$, R^8-NCO, $-CN$, $-R^8CN$,

$-NNC(=S)R^9$, $-R^8NNC(=S)R^9$, $-NO_2$, $-R^8NO_2$,

$$-C(O)N\begin{smallmatrix}R^{12}\\R^{13}\end{smallmatrix} \quad -R^{11}C(O)N\begin{smallmatrix}R^{12}\\R^{13}\end{smallmatrix} \quad -N\begin{smallmatrix}R^{12}\\R^{13}\end{smallmatrix}$$

$$-R^{11}N\begin{smallmatrix}R^{12}\\R^{13}\end{smallmatrix} \quad -OC(O)N\begin{smallmatrix}R^{12}\\R^{13}\end{smallmatrix} \quad -R^{11}OC(O)N\begin{smallmatrix}R_{12}\\R_{13}\end{smallmatrix} \quad \overset{O}{\underset{O}{\overset{\|}{-}S}}R^{12} \quad -R^{11}\overset{O}{\underset{O}{\overset{\|}{S}}}R^{12} \quad -O\overset{O}{\underset{O}{\overset{\|}{S}}}R^{12} \quad -R^{11}O\overset{O}{\underset{O}{\overset{\|}{S}}}R^{12}$$

10 $$-O\overset{O}{\underset{O}{\overset{\|}{S}}}OR^{12} \quad -R^{11}O\overset{O}{\underset{O}{\overset{\|}{S}}}OR^{12} \quad -B\begin{smallmatrix}R^{12}\\R^{13}\end{smallmatrix} \quad -R^{11}B\begin{smallmatrix}R^{12}\\R^{13}\end{smallmatrix} \quad -R^{11}B\begin{smallmatrix}OR^{12}\\OR^{13}\end{smallmatrix} \quad -B\begin{smallmatrix}OR^{12}\\OR^{13}\end{smallmatrix} \quad \overset{R^{12}}{-N}\overset{O}{\underset{}{\overset{\|}{-C}}}-R^{13}$$

$$\overset{R^{12}}{-R^{11}N}\overset{O}{\underset{}{\overset{\|}{-C}}}-R^{13} \quad \overset{R^{12}}{-N}\overset{O}{\underset{}{\overset{\|}{-C}}}-OR^{13} \quad \overset{R^{12}}{-R^{11}N}\overset{O}{\underset{}{\overset{\|}{-C}}}-OR^{13} \quad -\overset{O}{\overset{}{C}}-C\begin{smallmatrix}O\\R^{12}\end{smallmatrix}\overset{R^{14}}{\underset{R^{13}}{}} \quad -R^{11}\overset{O}{\overset{}{C}}-C\begin{smallmatrix}\\R^{12}\end{smallmatrix}\overset{R^{14}}{\underset{R^{13}}{}} \quad \overset{O}{\overset{}{-C}}\overset{R^{12}}{-N}\overset{O}{\underset{}{\overset{\|}{-C}}}-OR^{13}$$

$$\overset{O}{\overset{}{-R^{11}C}}\overset{R^{12}}{-N}\overset{O}{\underset{}{\overset{\|}{-C}}}-OR^{13} \quad -P\begin{smallmatrix}OR^{12}\\OR^{13}\end{smallmatrix} \quad -R^{11}P\begin{smallmatrix}OR^{12}\\OR^{13}\end{smallmatrix} \quad -OP\begin{smallmatrix}OR^{12}\\OR^{13}\end{smallmatrix} \quad -R^{11}OP\begin{smallmatrix}OR^{12}\\OR^{13}\end{smallmatrix} \quad -\overset{O}{\overset{\|}{P}}\begin{smallmatrix}OR^{12}\\OR^{13}\end{smallmatrix}$$

$$-R^{11}\overset{O}{\overset{\|}{P}}\begin{smallmatrix}OR^{12}\\OR^{13}\end{smallmatrix} \quad -O\overset{O}{\overset{\|}{P}}\begin{smallmatrix}OR^{12}\\OR^{13}\end{smallmatrix} \quad \text{or} \quad -R^{11}O\overset{O}{\overset{\|}{P}}\begin{smallmatrix}OR^{12}\\OR^{13}\end{smallmatrix}$$

in which R^8 is a linear or branched C_{1-20} alkyl, haloalkyl, alkenyl or haloalkenyl; a

15 linear or branched C_{3-20} alkynyl or haloalkynyl; a C_{3-12} cycloalkyl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; a C_{6-40} aryl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; or a C_{7-15} aralkyl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl;

12

each of R^9, R^{10}, and R^{11} is a hydrogen; a halogen; a linear or branched C_{1-20} alkyl, haloalkyl, alkenyl or haloalkenyl; a linear or branched C_{3-20} alkynyl or haloalkynyl; a C_{3-12} cycloalkyl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; a C_{6-40} aryl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; a C_{7-15} aralkyl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; or an alkoxy, an haloalkoxy, a carbonyloxy or a halocarbonyloxy; and

k is an integer from 1 to 10.

A norbornene addition polymer having a polar functional group produced using the method of the present embodiment includes at least 0.1-99.9 mol% of a norbornene-based monomer having a polar functional group, in which the norbornene having a polar functional group is composed of a mixture of endo and exo isomers and the deterioration of the catalytic activity by endo-isomers containing polar functional groups can be avoided and thus a composition ratio of the mixture is not critical for polymerization performance.

In accordance with the method of the present invention, a norbornene-based monomer and a catalyst are dissolved in a solvent or mixed with a solvent to prepare a norbornene-based polymer. The cyclic olefin polymer containing polar functional groups having a molecular weight of 100,000 or more can be prepared in a yield of 40% or higher. In order to fabricate an optical film using the cycloolefin polymer, the molecular weight of the cycloolefin polymer is preferably controlled to 100,000-1,000,000.

In conventional polymerization system, cyclic olefin polymers containing polar functional groups is prepared in a very low yield and in a low molecular weight, whereas the present method produces a high molecular weight of a cycloolefin polymer containing polar functional groups in a high yield.

The norbornene-based polymer containing polar functional groups prepared in accordance with the method of the present invention is transparent, has sufficient adhesion to metals or polymers containing different polar functional groups, thermal

stability and strength, and exhibits a low dielectric constant sufficient to be used as insulating electronic materials. The cyclic olefin polymer produced by the present invention has a desirable adhesion to substrates of electronic components without requiring a coupling agent, and at the same time, a sufficient adhesion to metal

5   substrates, e.g., Cu, Ag and Au. Further, the cyclic olefin polymer of the present invention exhibits desirable optical properties so that it can be used as materials for protective films of polarizing plates and electronic components such integrated circuits (ICs), printed circuit boards, multichip modules, and the like.

The polymer of the present embodiment can be used to produce an optical

10   anisotropic film capable of controlling a birefringence, which could not be produced with the conventional method.

A conformational unit of a general cyclic olefin has one or two stable rotation conditions, and thus can achieve an extended form such as polyamide having a rigid phenyl ring as a backbone. When a polar functional group is introduced into a

15   norbornene-based polymer with an extended form, the interaction between molecules increases compared to polymers having simple forms, and thus packing of molecules has a directional order, thereby producing optical and electronic anisotropy.

The birefringence can be controlled according to the type and the amount of polar functional group in the cyclic olefin polymer. In particular, the birefringence in a

20   direction through the film thickness is easily controlled, and thus the polymer of the present embodiment can be used to produce an optical compensation film for various modes of liquid crystal display (LCD).

The optical anisotropic film of the cyclic olefin polymer having a polar functional group can be prepared by a solution casting or can be prepared with a blend of one or

25   more cyclic olefin polymers.

In order to prepare a film by solution casting, it is preferable to introduce a cyclic olefin polymer in a solvent in amount of 5-95% by weight, and preferably 10-60% by weight, and stirring the mixture at room temperature. The viscosity of the prepared solution is 100-10,000 cps, and more preferably 300-8000 cps for solution casting. To

14

improve mechanical strength, heat resistance, light resistance, and manipulability of the film, additives such as a plasticizer, a anti-deterioration agent, a UV stabilizer or an antistatic agent can be added.

The optical anisotropic film thus prepared has a retardation value (R_{th}) of 70 to 1000 nm, as defined by the following Equation 1:

$$R_{th} = \Delta (n_y - n_z) \times d \tag{4}$$

where n_y is a refractive index of an in-plane fast axis measured at 550 nm, n_z is a refractive index toward thickness direction measured at 550 nm, and d is a film thickness.

The optical anisotropic film meets a refractive index requirement of $n_x \cong n_y < n_z$, in which n_x is a refractive index of an in-plane slow axis, n_y is a refractive index of an in-plane fast axis, and n_z is a refractive index toward thickness direction, and thus can be used as a negative C-plate type optical compensation film for LCD.

Hereinafter, the present invention will be described in more detail with reference to the following Examples. However, these Examples are given for the purpose of illustration and are not to be construed as limiting the scope of the invention.

In the following Preparation Examples and Examples, all operations handling compounds sensitive to air or water were carried out using standard Schlenk technique or dry box technique. Nuclear magnetic resonance spectra were obtained using Bruker 400 and 600 spectrometers. A molecular weight and a molecular weight distribution of a polymer were determined by gel permeation chromatography (GPC) using standard polystyrene samples. Toluene, hexane and Et_2O were distilled and purified in sodium/benzophenone and CH_2Cl_2 was distilled and purified in CaH_2.

Preparation Example 1

Preparation of 5-norbornene-2-carboxylic acid methylester

Dicyclopentadiene (DCPD, Aldrich Co., Ltd., 256.5 mℓ, 1.9 mol), methyl acrylate (Aldrich Co., Ltd., 405 mℓ, 4.5 mol), and hydroquinone (3.2 g, 0.03 mol) were added to a 2

L high-pressure reactor and heated to 220℃. This reactor was stirred at 300 rpm for 5 hours, cooled and transported into a distillation flask. The mixture was distilled under reduced pressure at 1 torr using a vacuum pump at 50℃ to obtain a product (Yield: 57.6 %, exo/endo=58/42).

^{1}H-NMR (600MHz, CDCl$_3$), endo: δ 6.17 (dd, 1H), 5.91 (dd, 1H), 3.60 (s, 3H), 3.17 (b, 1H), 2.91 (m, 1H), 2.88 (b, 1H), 1.90 (m, 1H), 1.42 (m, 2H), 1.28 (m, 1H); exo: δ 6.09 (m, 2H), 3.67 (s, 3H), 3.01 (b, 1H), 2.88 (b, 1H), 2.20 (m, 1H), 1.88 (m, 1H), 1.51 (d, 1H), 1.34 (m, 2H).

Preparation Example 2

Preparation of 5-norbornene-2-allylacetate

DCPD (Aldrich Co., Ltd., 248 ㎖, 1.852 ㏖), allylacetate (Aldrich Co., Ltd., 500 ㎖, 4.63 ㏖), and hydroquinone (0.7 g, 0.006 ㏖) were added to a 2 L high-pressure reactor and heated to 190℃. This reactor was stirred at 300 rpm for 5 hours, cooled and transported into a distillation flask. The mixture was distilled twice under reduced pressure at 1 torr using a vacuum pump at 56℃ to obtain a product (Yield: 30 %, exo/endo=57/43).

^{1}H-NMR (300MHz, CDCl$_3$) : δ6.17 ~5.91 (m, 2H), 4.15 ~ 3.63 (m, 2H), 2.91 ~ 2.88 (m, 2H), 2.38 (m, 1H) , 2.05 (s, 3H), 1.83 (m, 1H), 1.60 ~ 1.25 (m, 2H) , 0.57 (m, 1H).

Preparation Example 3

Preparation of [HP(Cy)$_3$][Cl]

P(Cy)$_3$ (2.02 g, 7.2 mmol) was dispersed in Et$_2$O (150 mL) in a 250 mL Schlenk flask. Then, HCl (14.4 mL, 1.0 M in ether) was added to the solution at room temperature to give a white solid. After stirring for about 20 minutes, the solid was filtered through a glass filter and washed three times with Et$_2$O (80 mL). Thereafter, the residual solvent was removed at room temperature in vacuum to obtain [HP(Cy)$_3$][Cl] (86%, 1.95 g).

^{1}H-NMR (600MHz, CD$_2$Cl$_2$) : δ7.02 ~6.23 (d, 1H, J$_{H-P}$=470 Hz), 2.56 ~ 1.30 (m, 33H); ^{13}C-NMR (600MHz, CD$_2$Cl$_2$) : δ28.9 (d), 28.5 (d), 26.8 (d), 25.6 (s). ^{31}P-NMR (600MHz, CD$_2$Cl$_2$) :   δ 22.98 (d, J$_{P-H}$=470 Hz).

Preparation Example 4

Preparation of [HP(n-Bu)$_3$][Cl]

P(Cy)$_3$ (2.0 g, 10.0 mmol) was dissolved in Et$_2$O (150 mL) in a 250 mL Schlenk flask. Then, HCl (20.0 mL, 1.0 M in ether) was added to the solution at room temperature to give a white solid. After stirring for about 20 minutes, the solid was filtered through a glass filter and washed three times with Et$_2$O (80 mL). Thereafter, the residual solvent was removed at room temperature in vacuum to obtain [HP(n-Bu)$_3$][Cl] (90%, 2.15 g).

Preparation Example 5

Preparation of [HP(Cy)$_3$][B(C$_6$F$_5$)$_4$]

[Li][B(C$_6$F$_5$)$_4$] (1.0 g, 1.46 mmol) was suspended in CH$_2$Cl$_2$ (20 mL) in a 100 mL Schlenk flask and the CH$_2$Cl$_2$ (20 mL) solution of [HP(Cy)$_3$][Cl] (0.56 g, 1.75 mmol) prepared in Preparation Example 3 was slowly added thereto at room temperature. After stirring for 1 hour, the resulting slurry was filtered using a glass filter, the solvent was removed in vacuum until the volume of the solvent is 5 mL, the resultant was cooled to -78℃ and diethylether (30 mL) was added thereto to recrystalize.   Then, the solution was removed, the resultant was washed three times with diethylether (30 mL), the solvent was removed in a vacuum at room temperature to obtain [HP(Cy)$_3$][B(C$_6$F$_5$)$_4$] (90%, 1.26 g).

^{1}H-NMR (600MHz, CD$_2$Cl$_2$) : δ5.32 ~4.65 (d, 1H, J$_{H-P}$=440 Hz), 2.43 ~ 1.33 (m, 33H); ^{13}C-NMR (600MHz, CD$_2$Cl$_2$) : δ149.7, 148.1, 139.7, 139.2, 138.1, 138.0, 137.8, 136.2, 125.1, 124.9, 29.0, 28.8, 26.7 (d), 25.4 (s). ^{31}P-NMR (600MHz, CD$_2$Cl$_2$) :   31.14 (d, J$_{P-H}$=440 Hz). ^{19}F-NMR (600MHz, CD$_2$Cl$_2$) : -130.90, -161.51, -163.37.

Preparation Example 6

Preparation of [HP(n-Bu)$_3$][B(C$_6$F$_5$)$_4$]

[Li][B(C$_6$F$_5$)$_4$] (1.0 g, 1.46 mmol) was suspended in CH$_2$Cl$_2$ (20 mL) in a 100 mL Schlenk flask and the CH$_2$Cl$_2$ (20 mL) solution of [HP(n-Bu)$_3$][Cl] (0.42 g, 1.75 mmol) prepared in Preparation Example 4 was slowly added thereto at room temperature. After stirring for 1 hour, the resulting slurry was filtered using a glass filter, the solvent was removed in vacuum until the volume of the solvent is 5 mL, the resultant was cooled to -78℃ and diethylether (30 mL) was added thereto to recrystalize. Then, the solution was removed, the resultant was washed three times with diethylether (30 mL), the solvent was removed in a vacuum at room temperature to obtain [HP(Cy)$_3$][B(C$_6$F$_5$)$_4$] (87%, 1.12g).

Example 1
Polymerization of 5-norbornene-2-carboxylic methylester

5-norbornene-2-carboxylic methylester prepared according to Preparation Example 1 (MENB (10 mL, 55.6 mmol) was added to a 250 mL Schlenk flask. A (Pd(OAc)$_2$)(OAc=acetate, 2.5 mg, 11 μmol) and [HP(Cy)$_3$][B(C$_6$F$_5$)$_4$] (21.1 mg, 22 μmol) were added into a 250 mL Schlenk flask and dissolved in CH$_2$Cl$_2$ (1 mL). Then, a catalyst solution was added to the monomer solution via a syringe at 90℃. Polymerization reaction was carried out at 90℃ for 10 hours, and 50 mL of toluene was added thereto to dissolve the polymer. Thereafter, the resulting solution was added into an excess amount of ethanol to obtain white polymer precipitates. The precipitates were filtered through a glass filter to recover a polymer. The polymer was dried in a vacuum oven at 80℃ for 24 hours to obtain 5-norbornene-2-carboxylic methylester polymer (8.4 g: 80.5% by weight based on the total weight of used monomers). The weight average molecular weight (Mw) of the polymer was 200,400 and Mw/Mn was 2.02.

Examples 2 to 8
Polymerization of 5-norbornene-2-allylacetate

Polymers of 5-norbornene-2-allylacetate were prepared by changing the molar ratios of [HP(Cy)$_3$][B(C$_6$F$_5$)$_4$] to Pd(OAc)$_2$ to 2:1, 1:1, 2:3, 1:2, 1:4 and 1:8.

5-norbornene-2-allylacetate prepared according to Preparation Example 2 (4 mL, 24.7 mmol) and toluene (12 mL) were added to a 100 mL Schlenk flask, and a catalyst solution prepared by dissolving Pd(OAc)$_2$ (1.1 mg, 4.9 μ mol) and [HP(Cy)$_3$][B(C$_6$F$_5$)$_4$] having various equivalents in dichloromethane (1 mℓ) was added to the monomer solution. The polymerization was performed at 90 ℃ for 4 hours while stirring. The results are shown in Table 1 below.

Table 1

| | Pd(OAc)$_2$ (mg) | [HP(Cy)$_3$] [B(C$_6$F$_5$)$_4$] (mg) | Pd/B (molar ratio) | Yield | | Mw | Mw/Mn |
				[g]	[%]		
Example 2	1.1	2.4	2/1	1.77	43.2	333,400	2.11
Example 3	1.1	4.7	1/1	3.52	86.0	272,800	2.28
Example 4	1.1	7.1	2/3	3.82	93.2	260,000	2.56
Example 5	1.1	9.5	1/2	3.83	93.4	256,300	2.49
Example 6	1.1	19.0	1/4	3.80	90.5	221,600	2.45
Example 7	1.1	28.4	1/6	3.39	82.7	194,100	2.25
Example 8	1.1	38.0	1/8	3.30	80.5	193,200	2.20

Example 9

Preparation of norbornene carboxylic acid methylester / norbornene addition copolymer

Norbornene carboxylic acid methylester (16.74 g) and norbornene (4.44 g) as monomers and purified toluene (37 mℓ) as a solvent were added to a 250 mℓ Schlenk flask. Pd(OAc)$_2$ (4.79 mg) and [HP(Cy)$_3$][B(C$_6$F$_5$)$_4$] (40.4 mg) dissolved in dichloromethane (2 mL) were added thereto, and the reaction mixture was stirred for 10 hours at 90 ℃. The resulting solution was added into an excess amount of ethanol to obtain white polymer precipitates. The precipitates were filtered through a glass filter to recover a copolymer. The copolymer was dried in a vacuum oven at 65 ℃ for 24 hours to obtain norbornene/norbornene carboxylic acid methylester copolymer (14.86 g,

yeild: 70.2% by weight based on the total weight of used monomers). The weight average molecular weight (Mw) of the polymer was 184,000 and Mw/Mn was 2.12.

Example 10

Preparation of norbornene carboxylic acid methylester/butylnorbornene addition copolymer

Norbornene carboxylic acid methylester (14.64 g) and butylnorbornene (6.14 g) as monomers and purified toluene (37 mℓ) as a solvent were added to a 250 mℓ Schlenk flask. $Pd(acac)_2$ (4.19 mg) and $[HP(Cy)_3][B(C_6F_5)_4]$ (32.8 mg) dissolved in dichloromethane (2 mℓ) were added thereto, and the reaction mixture was stirred for 10 hours at 90℃. The resulting solution was added into an excess amount of ethanol to obtain white polymer precipitates. The precipitates were filtered through a glass filter to recover a copolymer. The copolymer was dried in a vacuum oven at 65℃ for 24 hours to obtain butylnorbornene/norbornene carboxylic acid methylester copolymer (13.7 g, yeild: 65.9% by weight based on the total weight of used monomers). The weight average molecular weight (Mw) of the polymer was 157,000 and Mw/Mn was 2.13.

Example 11

5-norbornene-2-allylacetate/butylnorbornene addition copolymer (catalyst: Pd(acac)₂)

5-norbornene-2-allylacetate (8.2 g) and butylnorbornene (3.2 g) as monomers and purified toluene (36 mℓ) as a solvent were added to a 250 mℓ Schlenk flask. A catalyst solution prepared by dissolving $Pd(OAc)_2$ (3.2mg) and $[HP(Cy)_3][B(C_6F_5)_4]$ (27.0 mg) in dichloromethane (2 mℓ) was added thereto, and the reaction mixture was stirred for 4 hours at 90℃. The resulting solution was added into an excess amount of ethanol to obtain white polymer precipitates. The precipitates were filtered through a glass filter to recover a copolymer. The copolymer was dried in a vacuum oven at 65℃ for 24 hours to obtain butylnorbornene/norbornene carboxylic acid butyl ester copolymer (9.30 g, yield: 81.7% by weight based on the total weight of used monomers). The

20

weight average molecular weight (Mw) of the polymer was 218,300 and Mw/Mn was 3.52.

Comparative Example 1

Polymerization of 5-norbornene-2-carboxylic acid

5-norbornene-2-carboxylic acid (10 g) and [Pd(C$_6$H$_5$CN)Cl$_2$]$_2$ (100 mg) were added to a flask and reacted at 140℃ for 10.5 hours to obtain a polymer (5.75 g) having a molecular weight of 1129.

Comparative Example 2

Polymerization of 5-norbornene-2-methyl-decanyl acetate

5-norbornene-2-methyl-decanyl acetate (1.03 g, 3.7 mmol) was added to a Schlenk flask, and [(Allyl)PdCl]$_2$ (13.15 mg, 3.60*10^{-2} mmol) and AgSbF$_6$ (35 mg, 10.1*10^{-2} mmol) were added to another flask, and chlorobenzene (2 mL) was added thereto. AgCl precipitate was filtered, and the resultant was added to the monomer at room temperature and reacted for 24 hours. The weight average molecular weight (Mw) of the polymer was 58,848 and Mw/Mn was 1.01 g (98%).

Comparative Example 3

Polymerization of 5-norbornene-2-allylacetate

5-norbornene-2-allylacetate (5.0 g, 30 mmol) and Li[B(C$_6$F$_5$)$_4$]·2.5Et$_2$O were added to a Schlenk flask. A solution prepared by dissolving [(Allyl)PdCl]$_2$ (0.55 mg, 0.0015 mmol) and P(Cy)$_3$ (0.84 mg, 0.0030 mmol) in toluene (0.1 mL) was added to the monomer. The mixture was reacted at 65℃ for 4 hours to obtain a polymer (0.25 g (5%)).

Examples 12 and 13

Preparation of optical anisotropic film

Each of the polymers prepared in Examples 1 and 2 was mixed with a solvent to form a coating solution as shown in Table 2. The coating solutions were cast on a glass substrate using a knife coater or a bar coater, and then the substrate was dried at room temperature for 1 hour and further dried under a nitrogen atmosphere at 100℃ for 18 hours. The glass substrate was kept at -10℃ for 10 seconds and the film on the

glass plate was peeled off to obtain a clear film having an uniform thickness. The thickness deviation of the film was less than 2%. The thickness and the light transmittance of the obtained film were shown in Table 2

Table 2

	Composition of film solution		Physical properties of film	
	Polymer (parts by weight)	Solvent (parts by weight)	Thickness (μm)	Light transmittance (%)
Example 12	Polymer prepared in Example 1	THF 560	114	92
Example 13	Polymer prepared in Example 2	CH$_2$Cl$_2$ 360 and TOLUENE 200	120	92

In Table 2, THF is tetrahydrofurane.

Experimental Example 1

Measurement of optical anisotropy

For clear films produced in Examples 12 and 13, a refractive index n was measured using an Abbe refractometer, an in-plane retardation value Re was measured using an automatic birefringence analyzer (available from Oji Scientific Instrument; KOBRA-21 ADH), and a retardation value R_θ was measured when the angle between incident light and the film surface was 50° and a retardation value R_{th} between the direction through the film thickness and the in-plane x-axis was calculated using Equation (2):

$$R_{th} = \frac{R_\theta \times \cos \theta_f}{\sin^2 \theta_f}$$

(2).

A refractive index difference (n_x-n_y) and a refractive index difference (n_y-n_z) were calculated by dividing R_e and R_{th} by the film thickness. (n_x-n_y), R_θ, R_{th} and (n_y-n_z) of each clear film were indicated in Table 3.

Table 3

	n (refractive index)	$(n_x-n_y) \times 10^3$	$R_{th}(nm/\mu m)$	$(n_y-n_z) \times 10^3$
Example 12	1.52	0.008	2.32	-
Example 13	1.50	0.009	2.13	2.13

When films were covered with a triacetate cellulose film having $n_y > n_z$, R_Θ values of all cyclic olefin films increased, which indicates that R_{th} of a cyclic olefin film is produced due to a negative birefringence ($n_y > n_z$) in a direction through the film thickness.

[Effect of the Invention]

According to the olefin polymerization method, deactivation of a catalyst due to a polar functional group of a monomer can be prevented, and thus a polyolefin having a molecular weight of equal to or greater than 100,000 can be prepared with a polymerization yield of equal to or greater than 60%, and the ratio of catalyst to monomer can be in the range of 1/5000 to 1/20,000 due to good activity of the catalyst, and thus removal of catalyst residues is not required.

<u>What is claimed is:</u>

1. A method of producing cyclic olefin polymers having polar functional groups, which comprises:

preparing a catalyst mixture including:

5   i) a procatalyst represented by formula (1) containing a Group 10 metal;

ii) a cocatalyst represented by formula (2) including a salt compound which comprises phosphonium; and

addition-polymerizing cyclic monomers having polar functional groups in the presence of an organic solvent and the catalyst mixture, at a temperature of 80-150 ℃:

10      $(R^0)_x(R^1)_yM$ (1)

wherein R^0 and R^1 are each independently a hydrogen; a halogen; a linear or branched C_{1-20} alkyl or alkenyl; an optionally substituted C_{5-12} cycloalkyl; an optionally substituted C_{6-40} aryl; an optionally substituted C_{7-15} aralkyl; a linear or branched C_{1-20} heteroalkyl or heteroalkenyl including one hetero atom selected from the group

15   consisting of Si, Ge, S, O and N; a C_{6-40} heteroaryl or C_{7-15} heteroaralkyl including one hetero atom selected from the group consisting of Si, Ge, S, O and N; a linear or branched C_{1-20} haloalkyl or haloalkenyl; a linear or branched C_{3-20} haloalkynyl; and an optionally substituted C_{6-40} haloaryl, wherein each substituent is a halogen or a C_{1-20} haloalkyl;

20   M is a Group 10 metal; and

x and y are each independently an integer from 1 to 2, and

$[H-P(R^2)_{3-a}[X(R^{2'})_b]_a][Ani]$ (2)

wherein a is an integer from 0 to 3;

X is O, S, Si, or N;

25   b is 1 if X is O or S, 2 if X is N, and 3 if X is Si;

R^2 and $R^{2'}$ are each independently a hydrogen; a linear or branched C_{1-20} alkyl, alkoxy, allyl, alkenyl or vinyl; an optionally substituted C_{3-12} cycloalkyl; an optionally substituted C_{6-40} aryl; an optionally substituted C_{7-15} aralkyl; a C_{3-20} alkynyl; a tri(linear or branched C_{1-10} alkyl)silyl; a tri(linear or branched C_{1-10} alkoxy)silyl; a tri(optionally

substituted C_{3-12} cycloalkyl)silyl; a tri(optionally substituted C_{6-40} aryl)silyl; a tri(optionally substituted C_{6-40} aryloxy)silyl; a tri(linear or branched C_{1-10} alkyl)siloxy; a tri(optionally substituted C_{3-12} cycloalkyl)siloxy; or a tri(optionally substituted C_{6-40} aryl)siloxy, in which each substituent is a halogen or C_{1-20} haloalkyl; and

5   [Ani] is an anion capable of weakly coordinating to the metal M of Formula 1 and is selected from the group consisting of borate, aluminate, $[SbF_6]$-, $[PF_6]$-, $[AsF_6]$-, perfluoroacetate($[CF_3CO_2]$-),   perfluoropropionate($[C_2F_5CO_2]$-), perfluorobutyrate($[CF_3CF_2CF_2CO_2]$-),   perchlorate($[ClO_4]$-), p-toluenesulfonate($[p-CH_3C_6H_4SO_3]$-), $[SO_3CF_3]$-, boratabenzene, and carborane

10 optionally substituted with a halogen.

2.   The method of claim 1, wherein the borate or aluminate of formula (2) is an anion represented by formula (2a) or (2b):

$[M'(R^3)_4]$ (2a)

15     $[M'(OR^3)_4]$ (2b)
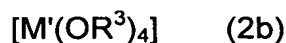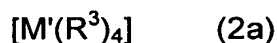
wherein M' is boron or aluminum;

R^3 is a halogen; a linear or branched C_{1-20} alkyl or alkenyl optionally substituted with a halogen; a C_{3-12} cycloalkyl optionally substituted with a halogen; a C_{6-40} aryl optionally substituted with a hydrocarbon; a C_{6-40} aryl optionally substituted with a linear

20 or branched C_{3-20} trialkylsiloxy or a linear or branched C_{18-48} triarylsiloxy; and a C_{7-15} aralkyl optionally substituted with a halogen.

3.   The method of claim 1, wherein a molar ratio of the cocatalyst to the procatalyst comprising Group 10 transition metal is 0.5-10:1.

25

4.   The method of claim 1, wherein the catalyst mixture is supported on a fine particulate support.

5.   The method of claim 4, wherein the fine particulate support is silica, titania,

silica/chromia, silica/chromia/titania, silica/alumina, aluminum phosphate gel, silanized silica, silica hydrogel, montmorillonite clay or zeolite.

6. The method of claim 1, wherein the catalyst mixture is dissolved in an organic solvent selected from the group consisting of dichloromethane, dichloroethane, toluene, chlorobenzene and a mixture thereof.

7. The method of claim 1, wherein the total amount of the organic solvent is 50-800% based on the weight of the total monomer in the monomer solution.

8. The method of claim 1, wherein the catalyst mixture comprises a metal catalyst complex composed of the procatalyst and the cocatalyst.

9. The method of claim 1, wherein the catalyst mixture is added in a solid phase to the monomer solution.

10. The method of claim 1, wherein the amount of the catalyst mixture is such that a molar ratio of the procatalyst to the total monomer is 1:2,500 to 1:200,000.

11. The method of claim 1, wherein the cyclic olefin polymer is a compound represented by Formula 3 below.
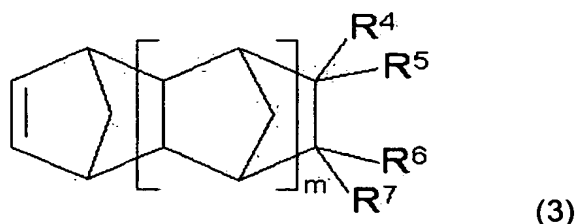

(3)

where m is an integer from 0 to 4;

at least one of R^4, R^5, R^6, and R^7 is a polar functional group, and the others are nonpolar functional groups, wherein R^4, R^5, R^6, and R^7 are bound to each other to form a saturated or unsaturated C_{4-12} cyclic group or a C_{6-24} aromatic ring;

wherein the nonpolar functional group is a hydrogen; a halogen; a linear or branched C_{1-20} alkyl, haloalkyl, alkenyl or haloalkenyl, a linear or branched C_{3-20} alkynyl or haloalkynyl; a C_{3-12} cycloalkyl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; a C_{6-40} aryl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; or a C_{7-15} aralkyl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; and

the polar functional group is a non-hydrocarbonaceous polar group having at least one O, N, P, S, Si or B and is $-OR^9$, $-OC(O)OR^9$, $-R^8OC(O)OR^9$, $-C(O)R^9$, $-R^8C(O)R^9$, $-OC(O)R^9$, $-R^8OC(O)R^9$, $-(R^8O)_k-OR^9$, $-(OR^8)_k-OR^9$, $-C(O)-O-C(O)R^9$, $-R^8C(O)-O-C(O)R^9$, $-SR^9$, $-R^8SR^9$, $-SSR^8$, $-R^8SSR^9$, $-S(=O)R^9$, $-R^8S(=O)R^9$, $-R^8C(=S)R^9$, $-R^8C(=S)SR^9$, $-R^8SO_3R^9$, $-SO_3R^9$, $-R^8N=C=S$, $-NCO$, R^8-NCO, $-CN$, $-R^8CN$,

$-NNC(=S)R^9$, $-R^8NNC(=S)R^9$, $-NO_2$, $-R^8NO_2$,
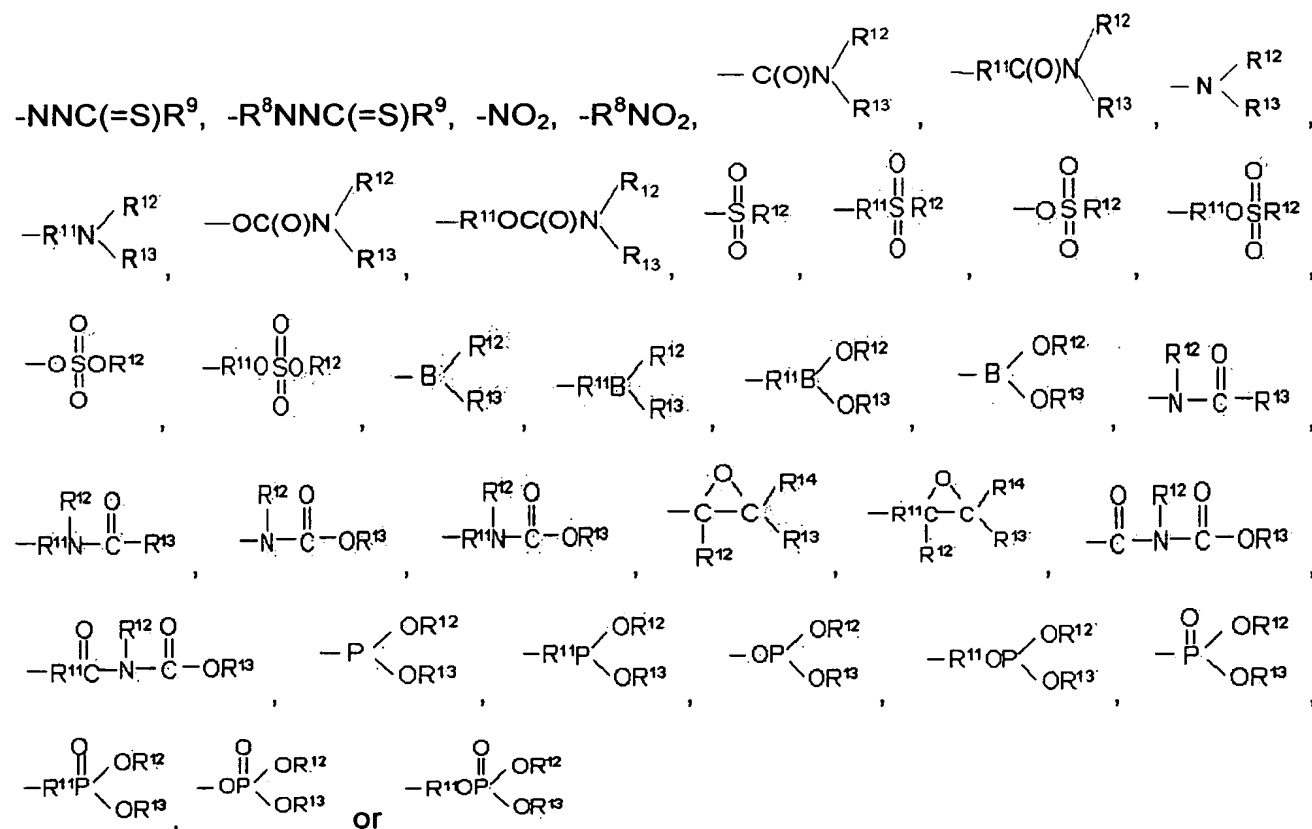
wherein R^8 is a linear or branched C_{1-20} alkyl, haloalkyl, alkenyl or haloalkenyl; a

linear or branched C_{3-20} alkynyl or haloalkynyl; a C_{3-12} cycloalkyl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; a C_{6-40} aryl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; or a C_{7-15} aralkyl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl;

each of R^9, R^{10}, and R^{11} is a hydrogen; a halogen; a linear or branched C_{1-20} alkyl, haloalkyl, alkenyl or haloalkenyl; a linear or branched C_{3-20} alkynyl or haloalkynyl; a C_{3-12} cycloalkyl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; a C_{6-40} aryl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; a C_{7-15} aralkyl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; an alkoxy, an haloalkoxy, a carbonyloxy or a halocarbonyloxy; and

k is an integer from 1 to 10.

12. The method of claim 1, wherein the monomer solution further comprises a cyclic olefin compound having no polar functional group.

13. The method of claim 1, wherein the cyclic olefin polymers having polar functional groups comprise a cyclic olefin homopolymer, a copolymer of cyclic olefin monomers having different polar functional groups, or a copolymer of a cyclic olefin monomer having a polar functional group and a cyclic olefin monomer having no polar functional group.

14. The method of claim 1, wherein a weight average molecular weight M_w of the cyclic olefin polymer having a polar functional group is 10,000-1,000,000.

15. A cyclic olefin polymer having polar functional groups and having a weight average molecular weight of equal to or greater than 100,000 prepared using the

method according to any one of claims 1 to 15.

16. An optical anisotropic film comprising the cyclic olefin polymer having the cyclic olefin polymer having polar functional groups and having a weight average molecular weight of equal to or greater than 100,000 prepared using the method according to any one of claims 1 to 15.

17. The optical anisotropic film of claim 16, which has a retardation value R_{th} represented by Equation (4) of 70-1000 nm:

$$R_{th} = \Delta (n_y - n_z) \times d \qquad (4)$$

where n_y is a refractive index of an in-plane fast axis measured at 550 nm;

n_z is a refractive index in a direction through the film thickness measured at 550 nm, and

d is a film thickness.

18. The optical anisotropic film of claim 16, which is a negative C-plate type optical compensation film for liquid crystal display, satisfying a refractive index requirement of $n_x \cong n_y < n_z$, in which n_x is a refractive index of an in-plane slow axis, n_y is a refractive index of an in-plane fast axis, and n_z is a refractive index in a direction through the film thickness.